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SEMICONDUCTOR THIN FILMS

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LEAR SIEGLER, INC.

RESEARCH LABORATORIES

SANTA MONICA, CALIFORNIA

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1.0 PREVIOUS PLANS FOR THE THIRD QUARTER

- 1.1 To test the small, glass ultra high vacuum system for deposition of germanium.
- 1.2 To make Hall measurements at a series of temperatures from 77° K to room temperature, and to plan for measurements of lifetime.
- 1.3 To flash evaporate doped silicon in an effort to deposit n type films.
- 1.4 To continue work on device preparation using the films deposited in high and ultra high vacua.
- 1.5 To deposit single crystal films on mica.
- 1.6 To start test depositions of conductors, resistors, and contact tabs on beryllia, fluorite, and mica.



## 2.0 ACCOMPLISHMENTS

### 2.1 Ultra High Vacuum

A simple ultra high vacuum system was built and used for deposition of germanium (Figure 1). Five depositions were made.

In run No. 1, the system, attached to the Veeco 4 inch vacuum system, was outgassed by placing the 8" x 1" silica tube in a tube furnace and heating to about 1000°C (temperature estimated by eye). In the tube were a fused silica supporting framework, a tungsten filament loaded with Ge, a tantalum sheet with hooks supporting a CaF<sub>2</sub> substrate, and Ba getters designed for use in vacuum tube manufacture. One of two Ba getters partly evaporated during the outgassing. When the pressure had dropped to  $2 \times 10^{-6}$  torr, after about 14 hours of outgassing, the tube was sealed off from the Veeco system and the pressure rose temporarily to  $3 \times 10^{-4}$  torr. The tube was then placed in the coil of an RF induction heater and the first getter evaporated. The pressure dropped to  $1 \times 10^{-7}$ . Getter No. 2 was then fired and the pressure dropped to  $4 \times 10^{-8}$ . The end of the tube was immersed in liquid nitrogen and the pressure dropped to  $2.4 \times 10^{-8}$ . The Ge and substrate were then heated by positioning the RF coil between them, and the RF power raised gradually. The pressure rose temporarily at each increase of power until evaporation started. Temperatures were estimated by eye. The substrate heater reached 800° while the Ge was at 900° so the coil was moved and power increased until



the Ge melted while the substrate heater was at about 600°. Evaporation continued for 10 minutes at a pressure of 3 to 4 x 10<sup>-6</sup>. On cooling, the pressure was 3 x 10<sup>-8</sup> and rose to 4 x 10<sup>-8</sup> on removing the liquid nitrogen. The deposit was polycrystalline.

In run No. 2, two grams of activated charcoal were inserted in place of the getters, and a stainless steel optical baffle was placed between the Ge and the outlet to the Veeco system. The small system was outgassed at 650° (thermocouple outside the silica tube) for 3 days and the attached gauge at 420° for a short time until the pressure dropped to 3 x 10<sup>-4</sup>. During seal off, the pressure rose to over 10<sup>-3</sup> but dropped, on cooling to room temperature, to 4 x 10<sup>-9</sup>. The pressure read 6 x 10<sup>-6</sup> as deposition started but rose to over 1 x 10<sup>-3</sup> by the end of the deposition and remained above 10<sup>-3</sup> for several hours after the power was turned off. The deposit was single crystal (Figure 2) with the familiar diffuse X.

In run No. 3, mica baffles were inserted between 1 gram of carbon, the evaporation framework, and the attached vacuum gauge. The carbon was outgassed at 820° while the Ge near the end of the tube furnace remained somewhat cooler. The gauge was outgassed at 450°. The pressure before seal off was 2 x 10<sup>-4</sup> with everything hot but, on shifting the tube in order to get at the intended seal off site, the pressure went over 10<sup>-3</sup> so it was shifted back until the pressure dropped to 6 x 10<sup>-4</sup> and sealed off with the



usual pressure rise to over  $10^{-3}$ . On cooling the pressure dropped to  $4 \times 10^{-9}$ . The mica had dehydrated and may have acted as a gas reservoir. The substrate heater was preheated to  $900^{\circ}\text{C}$  and deposition carried out with the substrate heater at about  $750^{\circ}$  and the pressure reading about  $2 \times 10^{-5}$ . The next morning the pressure was  $1.6 \times 10^{-6}$ . The deposit was polycrystalline.

In run No. 4, Vycor was used for baffles and Ti as the getter. The tube was outgassed at  $700^{\circ} - 795^{\circ}$  for 6 hours and at  $795^{\circ}$  for 16 more hours, the pressure dropping to  $4 \times 10^{-6}$ . The system was then tipped off. On cooling, the pressure dropped to  $5 \times 10^{-9}$ . During firing of the Ti getter, the pressure rose temporarily to  $6 \times 10^{-6}$  as the silica tube near the getter got red hot. The pressure then settled at  $2 \times 10^{-8}$ . During evaporation, the pressure could not be read because of electrical interference but was  $5 \times 10^{-8}$  immediately after the RF was turned off and  $6 \times 10^{-9}$  when the system had cooled down. The deposit was polycrystalline.

In run No. 5, no getter was used. The system was outgassed at  $750^{\circ}\text{C}$  for about 100 hours and tipped off. The pressure was  $4 \times 10^{-9}$  but rose to  $10^{-6}$  when the silica tube was flame heated to about  $800^{\circ}\text{C}$ . After cooling, the pressure settled at  $2 \times 10^{-8}$ . During deposition, the pressure was not read but after deposition it dropped, as cooling proceeded, from  $1.5 \times 10^{-7}$  to  $2 \times 10^{-8}$ . The deposit was partly polycrystalline but there was no detectable



diffuse X.

We shall repeat the depositions in a dynamic  $10^{-8}$  vacuum system which Vactite has promised to make available.

## 2.2 Electrical Measurement

Hall measurements were made on additional GaAs deposits using the circuit described in Quarterly Report No. 2.

<u>Sample</u>	<u>Type</u>	<u>r</u> (ohm-cm)	<u>R</u> (cm <sup>3</sup> /coul.)	<u>ρ</u> (cm <sup>2</sup> /vs)	<u>T</u> (°C)
J547A	p	22.4 140	55	2.5	22 -195
J559B	p	5.7 54	80 150	12.8 2.8	22 -195

Better contacts are needed. The present plan is to fire Ag pads (to which wires may be soldered) onto the substrate before depositing the semiconductor and then connect the pad to p or n semiconductor by vacuum depositing In or Sn respectively.

The circuit elements  $B_2$ , D, V, and  $R_6$  have been replaced by a Kiethly Model C 660 dc differential voltmeter with null adjustment and full scale readings from 0.1 mv to 500 v;  $B_1$  has been replaced by an Electronic Measurement Model C 636 constant current supply, 0.0015 ma to 220 ma. Sample geometries are shown in Figure 3. No work has yet been done on lifetime measurement.

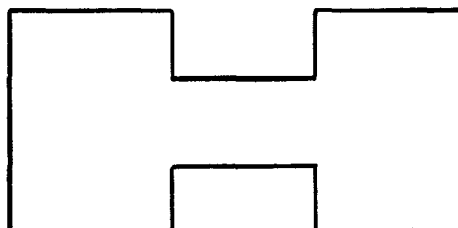


### 2.3 Deposition of Doped Silicon

Silicon was deposited, as single crystal films with the familiar diffuse X, from a filament onto both single crystal Si and single crystal BeO held at  $1145^{\circ}$ , and by flash evaporation onto Si. For both methods of evaporation and using either n or p type source material, the deposits were n type on n type Si and p type on p type Si. Further work with Si will be deferred.

### 2.4 Device Work

Previous experiments with Si and GaAs showed that thermally grown oxides on semiconductor surfaces form a potential barrier, and, if contacts are made between two Au, Sn or Al electrodes of dissimilar areas deposited on the oxide, rectification characteristics are obtained. Adapting this effect for a three-terminal device, a geometry of the deposited Ge film was chosen which, as shown below, provided two large outside areas for emitter and collector electrodes and a narrow middle region to function as a base.



Scale 10:1

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The Ge films were deposited on  $\text{CaF}_2$  single crystal substrates at  $10^{-6}$  torr. The films were 3000 - 5000 angstroms thick, p type, and single crystal by X-ray diffraction. The initial oxidizing treatment was performed in air for one hour at  $495^\circ\text{C}$ . This is about the maximum temperature at which the Ge films can be treated as the oxide starts to evaporate at higher temperatures. The effects of other ambients, such as dry and wet oxygen, ozone and ammonia, which will certainly give different characteristics to the Ge surface, will be investigated later. Pure Au was deposited for electrodes.

To obtain a base region width and spacing between the emitter and collector regions of the order of microns, thin wires were attached across an open window mask. Enamel coated Cu wire was tried first, but the best available thickness was 25 microns. Fused  $\text{SiO}_2$  threads of 3-5 micron diameter were also investigated. The final configuration and appearance of the assembly are shown in Figure 4. Electrical tests of this structure on a transistor curve tracer and a dc circuit revealed many problems of different origin.

1. Device Circuit Open

Poor adhesion of the Ge films to the  $\text{CaF}_2$  substrate resulted in peeling of the deposit, sometimes immediately after deposition, sometimes later during processing. The mismatch of the coefficients of thermal expansion of the two materials explains this defect. (The value for  $\text{CaF}_2$  is  $200 \times 10^{-7}$ , for Ge  $58 \times 10^{-7}$ .)



The defects have been more serious with thicker deposits.

2. Device Circuit Shorted

Shorts appeared as a result of inadequate masking. Even with the wires 25 microns thick, the Au vapors were able to creep under the wires and form unwanted interconnections between the electrodes.

3. Erratic and Unreproducible Characteristic Readings

These problems were caused by instability of the Ge surface when exposed to air. Improvement was observed after a light etch of the gap between electrodes by hydrogen peroxide - the recovery was unfortunately of very short duration.

In the second stage of this project, work was directed toward revision of the previous design to solve the above-mentioned difficulties. To improve the adhesion of the film to the substrate, single crystal sapphire with a coefficient of thermal expansion of  $87 \times 10^{-7}$  was used. A few trials with sapphire in the past did not result in single crystal formation, but at this stage of device development we used the sapphire substrate even though it meant sacrificing the single crystal structure. The second and third problems were solved simultaneously by changing the sequence of deposition. A continuous film of Au was deposited first and, to improve the adhesion, the substrate was maintained at  $280^{\circ}\text{C}$  during the deposition. This film, intended as electrodes for emitter and collector regions, was separated into two electrodes by



using an anodically etched W wire in a micromanipulator to scribe a line 2 - 4 microns wide through the film. Ge was evaporated through a circular mask symmetrically located over the scribed line. The substrate temperature for the Ge deposit was 325° C. The impedance of the Ge layer between the electrodes was 0.15 megohms. After oxidizing at 300° C in air for one hour, the base electrode was evaporated as a strip 5 mils wide symmetrically placed over the emitter-collector separating line. Leads of 4 mil Cu wire were attached by indium solder to the electrodes (Figure 5).

#### 2.5. Electrical Characteristics

The results of these tests are only the preliminary readings. Being concerned about the qualitative effect, the voltage-current characteristic at different bias was observed on the transistor curve tracer. The qualitative results can serve for optimizing the process and the critical parameters for quantitative evaluations (Figure 6).

Work on three terminal devices will be deferred in favor of work on forming junction diodes using thicker deposits of p on n Ge on sapphire and, if possible, on  $\text{CaF}_2$ .

#### 2.6 Deposition on Mica

Twenty-three deposits of Ge and GaAs were made on a total of 30 synthetic fluorophlogopite and natural muscovite substrates. Though fast deposition at about 1 micron per second resulted in melting of Ge, slow deposits were



single of crystal quality similar to deposits on  $\text{CaF}_2$  (Figure 7). However, the cleaved surfaces have steps, mica delaminates easily, and polishing is a formidable prospect, so the use of mica will not be pursued.

## 2.7 Passive Element Deposition

Nichrome resistors and Be-Cu conductors were deposited on sapphire and cleaved  $\text{CaF}_2$  in the production coater normally used to make thin film passive microcircuits. The films adhered well and functioned properly but were not tested for stability or reproducibility.

## 2.8 Fast Deposition

An alternative to higher vacuum, for producing deposits less contaminated by the vacuum chamber ambient, is faster deposition. Ge was deposited at 0.7 microns per second from a W basket through a moving slit. Higher rates could not be tried because of the limited capacity of the basket. A three strand filament dipping at each end into a cup of molten Ge was then tried hoping that capillary action would feed Ge onto the hotter filament (Figure 8), but the feed was not fast enough. Other arrangements will be tried.

## 2.9 Deposition of n Type Germanium

Deposition of n type Ge by co-evaporation of Sb and Ge has been an art practiced by Mr. Timper. A series of depositions was made using the Sb gun and freshly loaded W baskets of Ge to determine the range of deposition rate ratios which give n type deposits. The higher rates of Sb deposition have been investigated. Sb at 0.23 A/minute and Ge at 1000 A/minute gives an n



type deposit. If all the Sb is deposited, the concentration is  $1 \times 10^{19}/\text{cc}$ .

Higher relative rates of Sb give p type deposits; lower relative rates have yet to be investigated.



3.0 PLANS FOR THE FINAL QUARTER

- 3.1 To deposit Ge in a dynamic  $10^{-8}$  torr vacuum.
- 3.2 To make Hall measurements at intermediate temperatures.
- 3.3 To make diodes with thicker Ge films and deposit circuits.
- 3.4 To deposit Ge at microns per second.
- 3.5 To determine the range of Sb:Ge deposition rate ratios giving n type deposits.



## LIST OF ILLUSTRATIONS

- Figure 1. Glass System for Deposition in Higher Vacuum.
- Figure 2. Glancing Angle Oscillation X-Ray Diffraction Pattern of  $\text{Ge}/\text{CaF}_2$  Deposited in a System like that in Figure 1.
- Figure 3. Sample Structures for Hall and Resistivity Measurements.
- Figure 4. Assembly for Au/Ge Triodes (left); Germanium Deposit (right).
- Figure 5. Second Stage Assembly.
- Figure 6. a. Diode Characteristic between the Base and Collector.  
b. Backward Transfer Characteristic.  
c. Negative Resistance Characteristic of the Device.  
d. Grounded Emitter Characteristic.  
e. Forward and Backward Transfer Characteristic.  
f. Saturation Characteristic.
- Figure 7. Glancing Angle Oscillation X-Ray Diffraction Pattern of  $\text{Ge}/\text{mica}$ .
- Figure 8. Arrangement for Capillary Feeding of a Filament for Ge Evaporation.





FIGURE 1

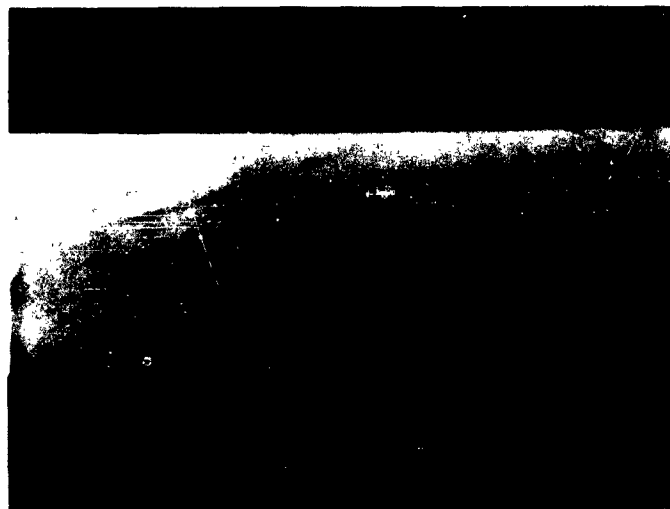
Glass system for deposition in higher vacuum

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**FIGURE 2**

Glancing angle oscillation X-ray diffraction pattern of Ge/CaF<sub>2</sub> deposited in a system like that in Figure 1 (UHV-2, film 1710)<sup>2</sup>



FIGURE 3

Sample structures for Hall and resistivity measurements

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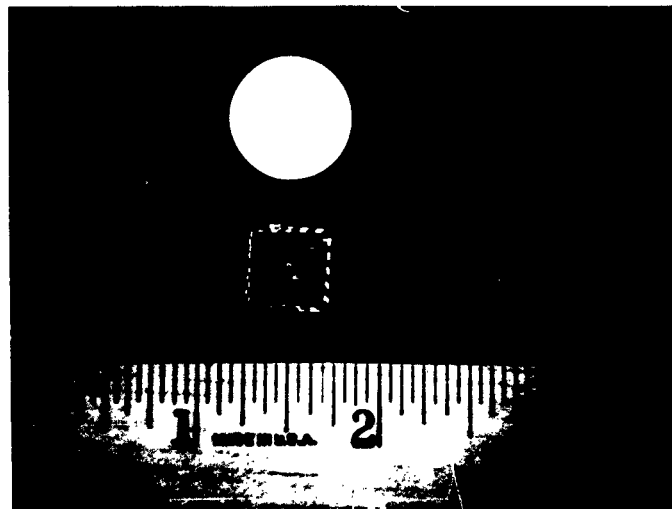


FIGURE 4

Assembly for Au/Ge triodes (left), germanium deposit (right).  
The germanium on the lower right is partly peeled.

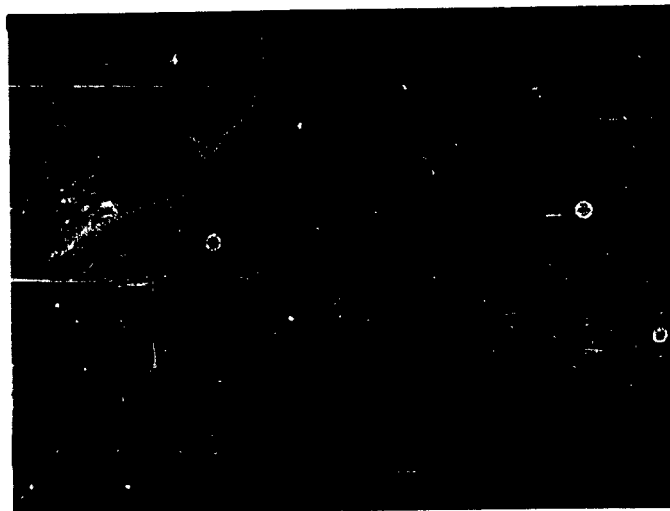


FIGURE 5

Second stage assembly

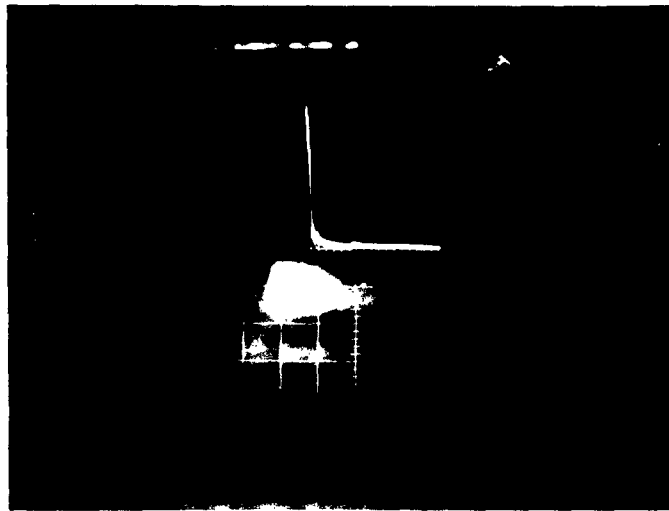


FIGURE 6 a.

Diode characteristic between the base and collector.  
Forward voltage drop 1.1 volt, forward current 0.4 ma.



FIGURE 6 b.

Backward transfer characteristic.  
Emitter voltage 0.1 volt per division, horizontal;  
collector current 1 ma per division, vertical;  
emitter current 0.5 ma per step.



FIGURE 6 c.

Negative resistance characteristic of the device.  
 Collector voltage 1 volt per division, horizontal;  
 collector current 1 ma per division, vertical;  
 Base current .007 ma (7 steps of .001 ma).



FIGURE 6 d.

Grounded emitter characteristic.  
 Collector voltage 1 volt per division, horizontal;  
 collector current 1 ma per division, vertical;  
 base current 0.1 ma per step.



FIGURE 6 e.

Forward and backward transfer characteristic.  
 1 volt per division, horizontal;  
 1 ma per division, vertical;  
 0.1 ma per step base current.



FIGURE 6 f.

Saturation characteristic  
 1 volt per division, horizontal;  
 1 ma per division, vertical;  
 1 volt per step base voltage.



FIGURE 7

Glancing angle oscillation X-ray diffraction pattern  
of Ge/mica. (J581C, film 1741).

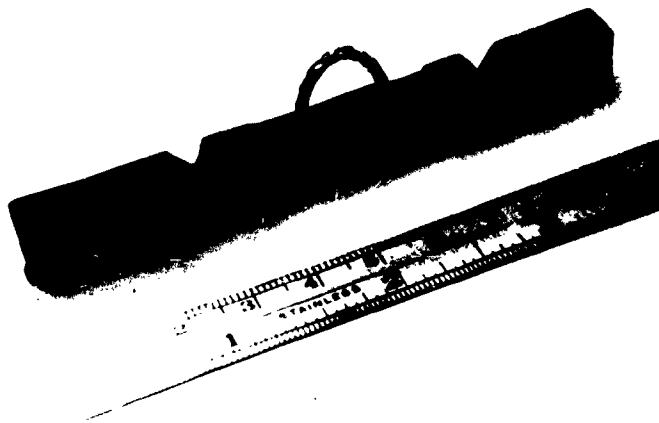


FIGURE 8

Arrangement for capillary feeding of a  
filament for Ge evaporation